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# Plasma-Sprayed Ceramic Coatings for Molten Metal Environments

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## Abstract

Coating porosity is an important parameter to optimize for plasma-sprayed ceramics which are intended for service in molten metal environments. Too much porosity and the coatings may be infiltrated by the molten metal causing corrosive attack of the substrate or destruction of the coating upon solidification of the metal. Too little porosity and the coating may fail due to its inability to absorb thermal strains. This study describes the testing and analysis of tungsten rods coated with aluminum oxide, yttria-stabilized zirconia, yttrium oxide, and erbium oxide deposited by atmospheric plasma spraying. The samples were immersed in molten aluminum and analyzed after immersion. One of the ceramic materials used, yttrium oxide, was heat treated at 1000°C and 2000°C and analyzed by X-ray diffractography and mercury intrusion porosimetry. Slight changes in crystal structure and significant changes in porosity were observed after heat treatments.

## Introduction

The use of plasma-sprayed ceramic materials as protective layers for use in molten metal processing equipment has several advantages. First, coatings of any kind allow for the de-coupling of the structural and chemical compatibility functions of components. Therefore, the structural material can be chosen to provide the needed mechanical properties for performing its function without regard to its molten metal compatibility while the coating material can be chosen for maximum molten metal compatibility since it need not perform the structural function. Plasma-sprayed ceramic coatings to contain molten uranium [1], copper alloys [2], titanium [3], aluminum [4] zirconium [5] and oxide ceramics [6] have been reported as having some successful applications. Some advantages of the plasma-sprayed coatings are the ability to produce a relatively thick layer (on the order of 0.1 – 1.0 mm) which is difficult to achieve using sprayed or brushed on liquid binder with suspended ceramic powder. The plasma-

sprayed materials also generally have superior thermal shock resistance as compared to a dense, sintered material as is typical of most bulk ceramics. The superior thermal shock resistance is due to the network of micro-cracks that result from the layered buildup of the plasma-sprayed coating and the stress relief cracks that form during cooling of the individual particles after impact.

The specific application for this study is for coatings that can withstand the chemical attack of molten plutonium metal. Materials examined were limited to stable oxide ceramics for this investigation. The materials chosen based on their low chemical reactivity with plutonium are yttrium oxide, erbium oxide, aluminum oxide, and zirconium oxide (cubic phase stabilized with yttrium oxide).

Two effects related to the structure of the coating are expected to play an important roll in the coating's survivability. In general, the more pores or microcracks which are present in a brittle ceramic, the more tolerant the coating is to thermal shock [7]. This is because the cracks or pores act as stress relief sites where thermal strains are relieved within the coating before large thermal stresses can cause cracks and subsequent coating failure. However, coating porosity provides the path for molten metal penetration. This penetration can cause difficulty in separating the solidified metal charge from the coating, can lead to chemical attack by the molten metal of the material underlying the coating, and can cause failure of the coating during solidification and cooling of the metal due to coefficient of thermal expansion mismatch. Finding the optimum coating structure which is thermal shock tolerant and prevents liquid penetration is key to success in this application.

## Experimental Procedure

The powders used for this experiment were:  $\text{Er}_2\text{O}_3$  product E-1015 from Cerac Inc. (Milwaukee, WI),  $\text{Y}_2\text{O}_3$  product Y-1055

from Cerac Inc.,  $\text{Al}_2\text{O}_3$  product 105NS from Sulzer Metco (US) Inc. (Westbury, NY),  $\text{ZrO}_2$  cubic phase stabilized with 8 mole percent  $\text{Y}_2\text{O}_3$ , product 204B-NS from Sulzer Metco (US) Inc. Figures 1-4 show SEM images of each powder used.

Each of the selected powders was sprayed under a high condition (high torch power resulting in high particle temperature and velocity) and a low condition. The plasma torch used for this experiment is the SG-100 from Praxair Surface Technologies (Indianapolis, IN). The torch anode was a model 730 and the cathode was model 720 with a model 112 gas injector. Particle temperature, velocity, and diameter at the substrate axial distance from the torch were measured using a DPV-2000 particle sensor from Tecnar Automation, Ltee. (St. Bruno, Quebec, Canada). The spray parameters used are given in Ref. 8. The average particle temperatures and velocities measured at the coating standoff distance were reported previously [8] and are shown in Table 1.

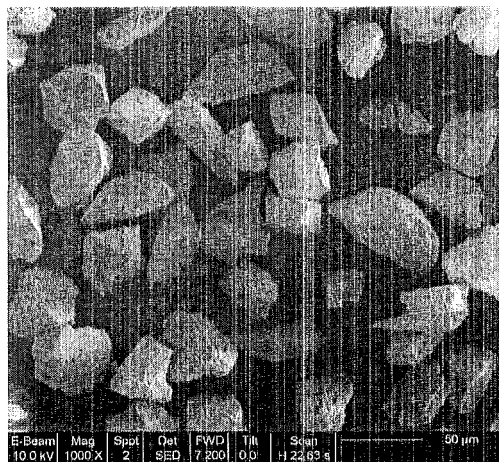


Figure 1: SEM image of  $\text{Y}_2\text{O}_3$  powder.

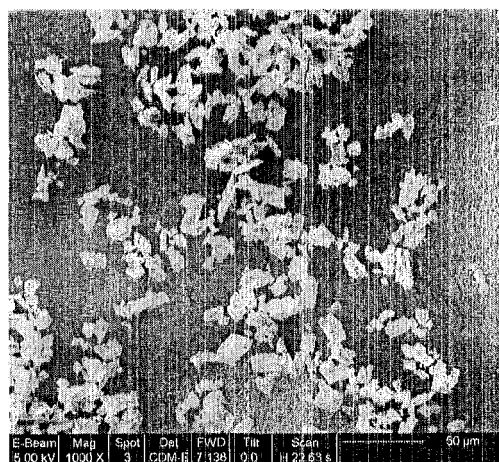


Figure 2: SEM image of  $\text{Er}_2\text{O}_3$  powder.

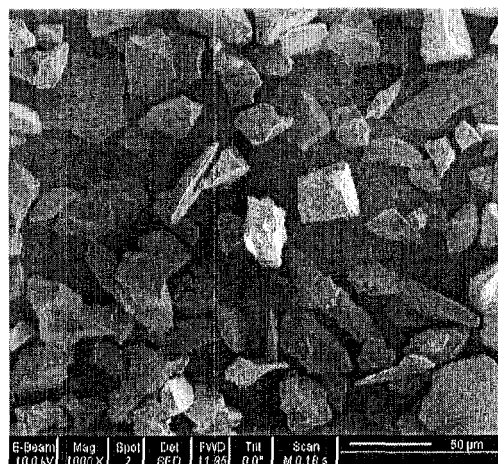


Figure 3: SEM image of  $\text{Al}_2\text{O}_3$  powder.

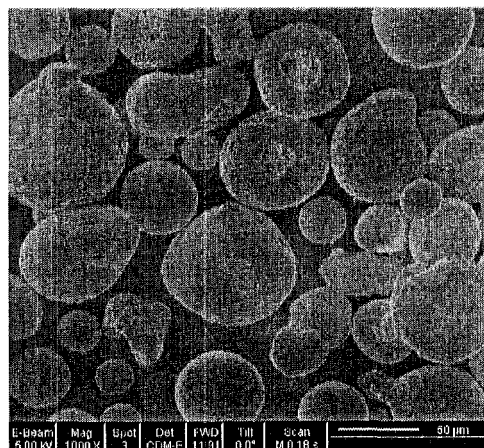


Figure 4: SEM image of YSZ powder.

Table 1: Particle velocity and temperature for samples sprayed under various conditions.

Sample	Velocity (m/s)	Temperature ( $^{\circ}\text{C}$ )
$\text{Al}_2\text{O}_3$ high	247	2326
$\text{Al}_2\text{O}_3$ low	194	2209
YSZ high	201	2544
YSZ low	145	2327
$\text{Y}_2\text{O}_3$ high	221	2600
$\text{Y}_2\text{O}_3$ low	169	2417
$\text{Er}_2\text{O}_3$ high	235	2356
$\text{Er}_2\text{O}_3$ low	185	2286

The test samples were solid tungsten rods 3.18 mm in diameter and 178 mm long. Eight rods were coated corresponding to the eight conditions listed in Table 1. The

rods were coated along approximately 70% of their length up to one of the ends. The circular ends of the rods were not coated. These rods are similar to components used in molten plutonium processing at Los Alamos National Laboratory.

After the rods were coated, they were subjected to thermal cycle testing. The samples were cycled from room temperature to 900°C a total of 10 times. The results of the thermal cycling tests have been reported previously [8].

The eight coated tungsten rods were immersed in molten 6061 aluminum after the thermal cycling was complete. The rods and aluminum were heated at a temperature increase of 15°C/minute up to the hold temperature of 750°C which is approximately 100°C above the 6061 aluminum liquidus temperature. The furnace used was an Oxy-gon model BC600 (Oxy-gon Industries, Inc., Epsom, NH). The furnace was evacuated and back filled with argon to local atmospheric pressure (78 kPa). The samples were held at 750°C for 30 minutes then cooled to room temperature at a rate of 15°C/minute. The rods and aluminum slug were sectioned and polished for examination by light microscopy.

The X-ray diffraction scans were acquired on a Scintag Pad V X-ray Diffractometer (Scintag Inc., Cupertino, CA, USA) using Cu K-alpha radiation on a theta-2 theta goniometer. Instrument conditions were 45 kV and 40 mA. Samples were mounted flush with the surface of the sample holder using clay. Scans were obtained from 10 to 90 degrees 2 theta, step size of 0.40 degrees 2 theta, with a count time of 3 seconds. The instrument manufacturer's software was used to identify peaks, which were then matched against the International Center for Diffraction Data (ICDD) database.

The mercury porosimetry measurements were taken using a Quantachrome Instruments PoreMaster 60 (Quantachrome Instruments, Boynton Beach, FL, USA). Instrument settings included a mercury contact angle of 140 degrees with surface tension of 480 erg/cm<sup>2</sup>. Each sample was analyzed at low pressure (5 to 50 psi), refilled at 5 psi, transferred to the high-pressure chamber, and analyzed at high pressure (20 to 60,000 psi). Data was processed using the Poremaster for Windows 4.00.13 software. Mercury porosimetry measurements quantify the volume versus diameter of open porosity in the sprayed samples.

## Results and Discussion

### Molten Aluminum Testing

Table 2 shows the results of testing in molten aluminum for the quality of contact between the coating and tungsten rod and the presence of cracks in the coating. The Er<sub>2</sub>O<sub>3</sub> coatings were both separated from the tungsten rod. The Y<sub>2</sub>O<sub>3</sub>, YSZ and Al<sub>2</sub>O<sub>3</sub> coatings sprayed under the low conditions showed good adhesion to the tungsten rod while the same materials

sprayed under high conditions showed a slight separation. The cracking behavior seen in these cross sectional views is qualitatively the same as was observed after the thermal cycle testing reported previously [8]. For Y<sub>2</sub>O<sub>3</sub>, YSZ and Al<sub>2</sub>O<sub>3</sub> the cracking was more severe for the samples sprayed under high conditions. Neither of the Er<sub>2</sub>O<sub>3</sub> samples exhibited any cracking. There was no molten aluminum penetration observed for any of the coatings tested.

*Table 2: Observations of coated samples after molten aluminum immersion.*

Sample	Contact	Cracking
Y <sub>2</sub> O <sub>3</sub> low	Good	Few
Y <sub>2</sub> O <sub>3</sub> high	Slight separation	Severe
Er <sub>2</sub> O <sub>3</sub> low	Separated	None
Er <sub>2</sub> O <sub>3</sub> high	Separated	None
YSZ low	Good	None
YSZ high	Slight separation	Several
Al <sub>2</sub> O <sub>3</sub> low	Good	Few, small
Al <sub>2</sub> O <sub>3</sub> high	Slight separation	Several

### X-ray diffraction results

Since Y<sub>2</sub>O<sub>3</sub> is expected to be the most resistant to chemical attack by molten plutonium and other reactive metals, further investigation of coating properties was limited to this material. Four samples were tested in the X-ray diffractometer to determine if any differences were present in crystal structure. The samples tested were the Y<sub>2</sub>O<sub>3</sub> as-sprayed samples for high and low conditions and these same samples after a furnace heat treatment at 1000°C for 0.5 hours. This heat treatment has been shown to transform any metastable monoclinic Y<sub>2</sub>O<sub>3</sub> to cubic Y<sub>2</sub>O<sub>3</sub> [9]. The as-sprayed sample sprayed under low conditions had a white color while the one sprayed under high conditions had a gray color. After heat treatment, both samples had a white color. X-ray diffraction results were very similar for all four samples. However, there was a small amount of metastable monoclinic Y<sub>2</sub>O<sub>3</sub> observed in the X-ray data in both of the as-sprayed samples. The heat-treated samples showed no sign of this metastable monoclinic Y<sub>2</sub>O<sub>3</sub> phase.

A small amount (up to 8%) of this metastable phase has also been observed by Gourlaouen et al. [10] while plasma spraying Y<sub>2</sub>O<sub>3</sub>. As was true in our experience, the metastable phase was not observed in the samples after heat treatment in Ref. 10. Since the color difference in the samples was between the two as-sprayed samples which each contain a slight amount of metastable phase, phase change is not responsible for the difference in sample color. Similar changes in color as a function of spray conditions for plasma-sprayed Y<sub>2</sub>O<sub>3</sub> have been reported previously [9] with a gray color at short substrate distances and a white/pink color at longer spray distances. As we have observed, Ref. 9 shows no dependence of color on crystal structure.

### Mercury intrusion porosimetry results

Mercury intrusion porosimetry results of pore diameter versus volume of pores is shown in Figs. 5-10. The pores were found to be bimodally distributed in size with one group ranging in diameter from 0.03  $\mu\text{m}$  to 0.2  $\mu\text{m}$  while the other group ranged from 5  $\mu\text{m}$  to 50  $\mu\text{m}$  in diameter. The percentage of total porosity in the coating of the small pores (0.03  $\mu\text{m}$  to 0.2  $\mu\text{m}$ ), large pores (5  $\mu\text{m}$  to 50  $\mu\text{m}$ ) and the combined total porosity is shown in Table 3.

### Coating sprayed under high conditions

In the as-sprayed condition, the coating sprayed under high conditions had a total porosity of 4.14% with 76% of the porosity in the small size and 24% in the large size. After heat treating the sample at 1000°C for 0.5 hours, the total porosity increased slightly from 4.14% to 4.86%. The small size porosity increased to 85% of the total while the large size porosity decreased to 15% of the total. The sample which was heat treated at 2000°C for 4.5 hours showed a significant decrease in total porosity from 4.14% to 1.33%. The small size pores were eliminated and the large size pores increased slightly from 1.01% to 1.33% of the total sample volume.

The increase in porosity after the 1000°C heat treatment may be due in part to a phase transformation from monoclinic to cubic  $\text{Y}_2\text{O}_3$  as suggested in Ref. 9. The monoclinic to cubic transformation, which results in a volume increase, has been shown to decrease fracture strength by crack formation in plasma-sprayed  $\text{Y}_2\text{O}_3$  coatings [10]. This crack formation will increase the small porosity of the material as was observed here. However, since the total amount of monoclinic phase present in the as-sprayed sample is quite low, this may not be the complete explanation. The large decrease of the small porosity during the 2000°C heat treatment can be attributed to sintering of the coating and has been observed previously [11]. The effect of this high temperature sintering mechanism on fracture strength has also been noted in Ref. 9.

### Coating sprayed under low conditions

The  $\text{Y}_2\text{O}_3$  coating sprayed under low conditions differed from the coating sprayed under high conditions. In the as-sprayed conditions, the coating sprayed under low conditions had a total porosity of 7.38% with 85% of this porosity in the small size and 15% in the large size. After heat treating at 1000°C for 0.5 hours, the total porosity decreased to 6.03% with 89% of this in the small size and 11% in the large size. The sample heat treated at 2000°C for 4.5 hours showed only a slight decrease in total porosity from 7.38% to 6.86%. All of the small porosity was eliminated by the 2000°C heat treatment as was the case for the sample sprayed under high conditions. The large porosity increased significantly from 1.1% to 6.86%.

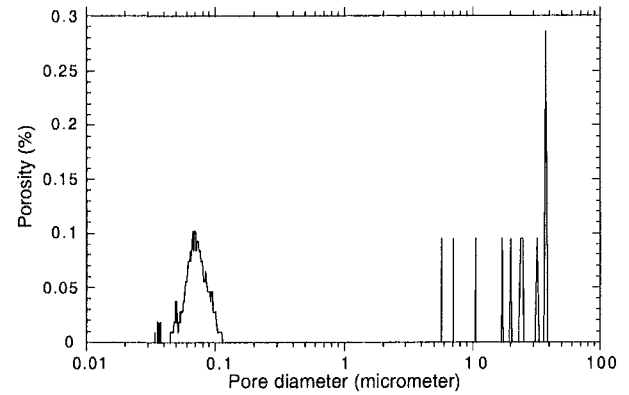


Figure 5: Pore distribution for  $\text{Y}_2\text{O}_3$  sample sprayed under high conditions.

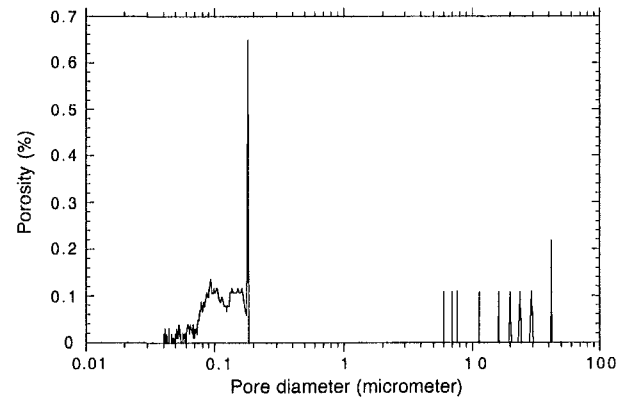


Figure 6: Pore distribution for  $\text{Y}_2\text{O}_3$  sprayed under low conditions.

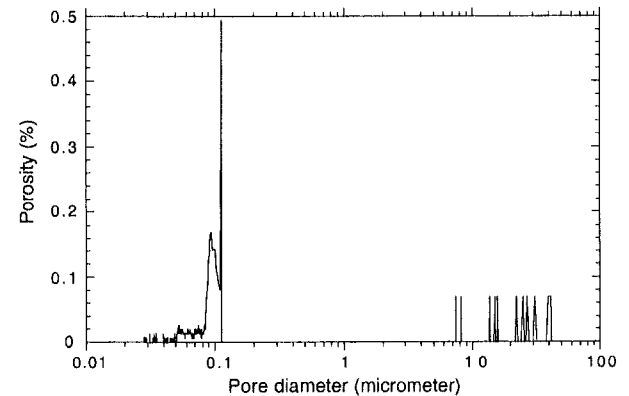


Figure 7: Pore distribution for  $\text{Y}_2\text{O}_3$  sprayed under high conditions and heat treated at 1000°C for 0.5 hours.

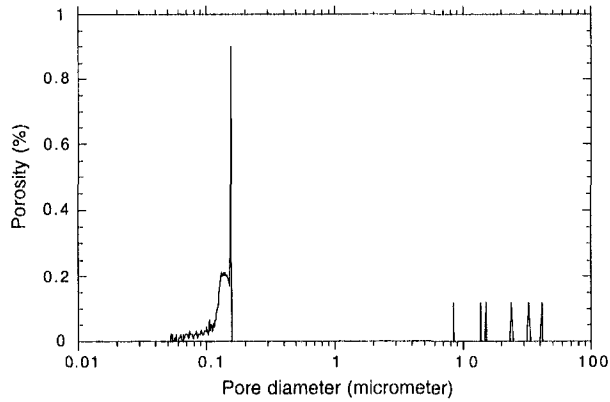


Figure 8: Pore distribution for  $Y_2O_3$  sprayed under low conditions and heat treated at  $1000^\circ C$  for 0.5 hours.

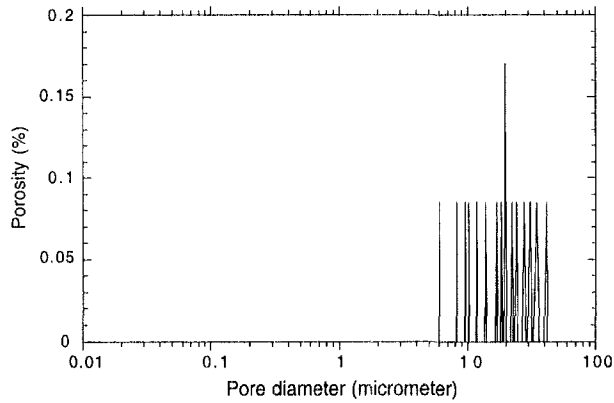


Figure 9: Pore distribution for  $Y_2O_3$  sprayed under high conditions and heat treated at  $2000^\circ C$  for 4.5 hours.

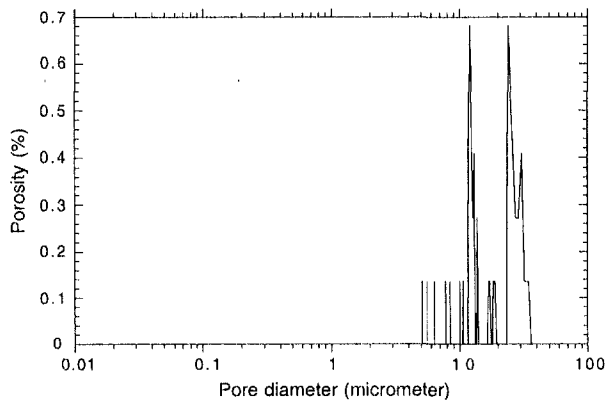


Figure 10: Pore distribution for  $Y_2O_3$  sprayed under low conditions and heat treated at  $2000^\circ C$  for 4.5 hours.

Table 3: Porosity measurements from mercury intrusion porosimetry.

Sample	large	small	total
$Y_2O_3$ high	1.01%	3.13%	4.14%
$Y_2O_3$ low	1.10%	6.28%	7.38%
$Y_2O_3$ high + $1000^\circ C$	0.74%	4.12%	4.86%
$Y_2O_3$ low + $1000^\circ C$	0.67%	5.36%	6.03%
$Y_2O_3$ high + $2000^\circ C$	1.33%	0%	1.33%
$Y_2O_3$ low + $2000^\circ C$	6.86%	0%	6.86%

The higher total porosity for the coating sprayed under the low conditions is consistent with many other studies which have determined the effect of spray conditions on oxide ceramic coating properties (for example Ref. 12, 13). The sample sprayed under low conditions and heat treated at  $2000^\circ C$  showed only a small decrease in total porosity. This is consistent with void coalescence which would cause a small change in total porosity along with a large change from small sized to large sized pores. There are likely many mechanisms at work during the sintering process and predictions of the densification are difficult as different materials behave in very different ways [14].

### Conclusions

This investigation of the properties of plasma-sprayed ceramics intended for use in molten metal environments has resulted in the following conclusions.

- Ceramic coatings sprayed under high conditions showed more tendency to separate from the tungsten rods after thermal cycling and molten aluminum testing.
- None of the ceramic coatings was penetrated by the molten aluminum during immersion.
- X-ray diffraction revealed a slight amount of metastable monoclinic  $Y_2O_3$  in the as sprayed samples for high and low conditions.
- No metastable monoclinic  $Y_2O_3$  was observed after a 0.5 hour heat treatment at  $1000^\circ C$ .
- Porosity in the as sprayed and  $1000^\circ C$  heat-treated  $Y_2O_3$  samples was found to be bimodal in size.
- After heat treatment at  $2000^\circ C$  for 4.5 hours, the small porosity was eliminated from the  $Y_2O_3$  samples.

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